PCCP

Published on 06 October 2000. Downloaded by SUNY GENESEO on 22/10/2014 18:52:59.

Free electron transfer from several phenols to radical cations of non-polar solvents

Mahalaxmi R. Ganapathi,[a] Ralf Hermann,[a] Sergei Naumov[b] and Ortwin Brede*[a]

[a] *University of Leipzig, Interdisciplinary Group Time-Resolved Spectroscopy, Permoserstrasse 15, D-04303 Leipzig, Germany. E-mail: brede@mpgag.uni-leipzig.de*
[b] *Institute of Surface Modification, Permoserstrasse 15, D-04303 Leipzig, Germany*

Received 20th July 2000, Accepted 24th August 2000
First published as an Advance Article on the web 6th October 2000

Electron-transfer reactions from phenols to parent radical cations of solvents were studied using pulse radiolysis. Phenols bearing electron-withdrawing, electron-donating and bulky substituents were investigated in non-polar solvents such as cyclohexane, n-dodecane, n-butyl chloride and 1,2-dichloroethane. The experiments revealed the direct, synchronous formation of phenoxyl radicals and phenol radical cations in all cases and in nearly the same relative amounts. This was explained by two competing electron-transfer channels which depend on the geometry of encounter between the parent solvent radical cations and the solute phenol molecules. The mechanism is analysed at a microscopic level, treating diffusion as a slow process and the local electron transfer as an extremely rapid event. Furthermore, the effect of various phenol substituents and solvent types on the electron-transfer mechanism and on the decay kinetics of the solute phenol radical cations was analysed. The results were further substantiated using a quantum chemical approach.

Introduction

The ionization of non-polar solvents such as saturated hydrocarbons and alkyl chlorides has been studied extensively in the last few decades. It has been found that this process creates uncorrelated pairs of electrons and molecular solvent radical cations in the nanosecond timescale, reaction (1a).[1] These parent solvent radical cations are stabilized by weak solvation. The free solvent parent cations are structured as a carbon skeleton with only sigma bonds where one electron is missing. Such species are metastable for a few hundred nanoseconds and constitute very efficient electron acceptors. After the addition of solutes with a lower ionization potential than the solvent, free electron transfer[2,3] takes place from these solute donors (S) to the parent radical cations ($RH^{\cdot+}$) in an exothermic, diffusion-controlled manner, as generally formulated in eqn. (1b). This reaction has been used for a huge variety of scavengers (S) to produce radical cations of the type $S^{\cdot+}$.[4]

$$RX \rightsquigarrow RX^{\cdot+},\quad e_{solv}^{-},\quad \ldots \qquad (1a)$$

$$RX^{\cdot+} + S \rightarrow S^{\cdot+} + RX \qquad (1b)$$

(RX is solvent where X = H or Cl)

The excess energy is used up in exciting the intramolecular vibrations in the reactant molecules. It was also found that the ionization potential difference between solute and solvent influences the vibrational overlap (Franck–Condon factor) of the reactant and product states, thus affecting the rate of electron transfer.[5]

Phenols have generated much interest, mainly due to their role as antioxidants in important biological and industrial processes. The mechanism of their action as antioxidants is primarily due to their ability to scavenge radicals by H-atom or any electron-transfer processes. Consequently, they are converted into phenoxyl radicals.[6–12] In this respect, because of their low ionization potential, phenols are solutes with good electron donor properties.

Early studies of phenols under non-protic conditions revealed phenoxyl radicals as the first observable products of one-electron-transfer oxidation.[13] In aqueous solution, phenol radical cations were hardly detected due to their low pK_a value and high instability. Hence, phenol radical cations in protic systems have been observed only in extremely acidic media.[14,15] Recently, pulse radiolysis of phenols (ArOH) in n-butyl chloride (n-C_4H_9Cl) at room temperature provided evidence for the direct observation of phenol radical cations.[16] It was found that the solvent radical cations reacted by electron transfer with the phenols to yield phenol radical cations eqn. (2a) as well as phenoxyl radicals eqn. (2b) in a parallel reaction.

$$ArOH + n\text{-}C_4H_9Cl^{\cdot+} \begin{cases} \rightarrow ArOH^{\cdot+} + n\text{-}C_4H_9Cl & (2a) \\ \rightarrow ArO^{\cdot} + H^{+}(n\text{-}C_4H_9Cl) & (2b) \end{cases}$$

Similar studies with naphthols (NpOH) and hydroxybiphenyls (ByOH) also revealed the generation of phenol-type radical cations ($NpOH^{\cdot+}$, $ByOH^{\cdot+}$) and phenoxyl-type radicals ($NpO^{\cdot}$, $ByO^{\cdot}$) in n-butyl chloride by an electron transfer analogous to reactions (2a) and (2b), with a bimolecular rate constant of around 10^{10} dm^3 mol^{-1} s^{-1}.[17] The same complex behaviour was found for aromatic thiols where both thiophenol radical cations and thiyl radicals appeared.[2] For the example of 4-hydroxythiophenol, the rapid formation of three different species, *viz.* radical cations, thiyl radicals and phenoxyl radicals, was found, which was interpreted by direct attacks of n-$C_4H_9Cl^{\cdot+}$ on the aromatic moiety and on the –SH (thiol) and –OH (hydroxy) groups respectively, prompting the hypothesis that the geometry of encounter between the parent radical cations and the solute molecules determines the product characteristics.[3]

The phenol radical cations ($ArOH^{\cdot+}$) thus produced are only stable up to a few hundred nanoseconds. They chiefly decay by deprotonation, yielding phenoxyl radicals ($ArO^{\cdot}$), eqn. (3a), although neutralization could be another pathway, eqn. (3b). The latter only seems to dominate in cases of

DOI: 10.1039/b005864p

This journal is © The Owner Societies 2000

View Article Online

Published on 06 October 2000. Downloaded by SUNY GENESEO on 22/10/2014 18:52:59.

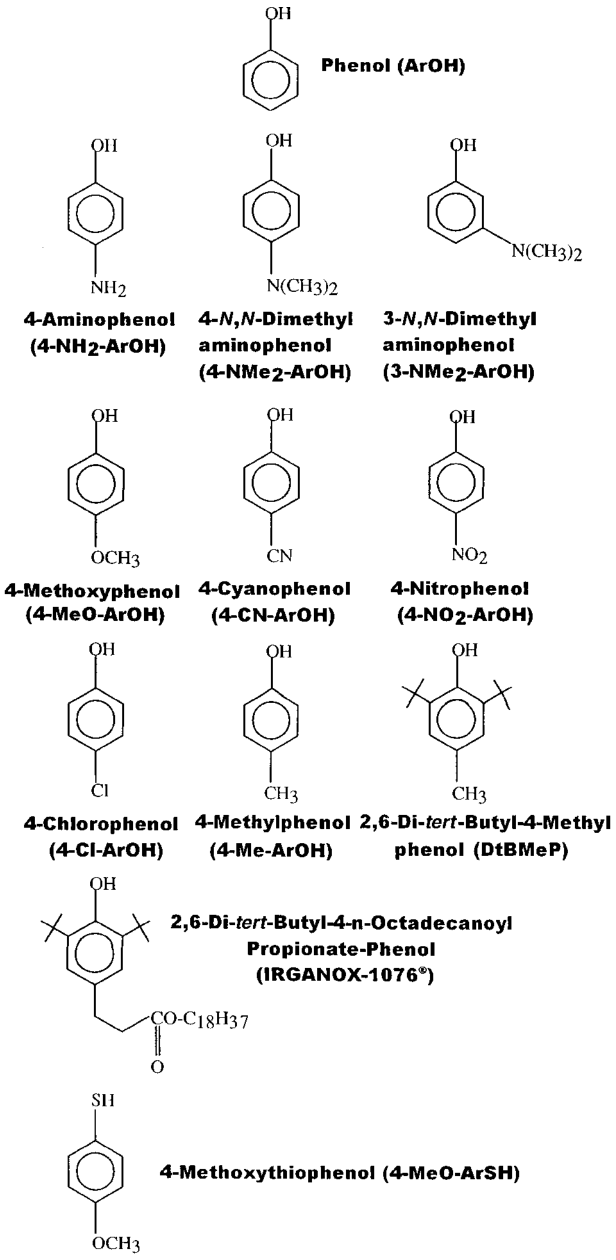

Fig. 1 Structures of phenols studied in the present investigation.

extremely electronically stabilized and highly substituted phenol radical cations produced by photoionization.[18]

$$\mathrm{ArOH^{\cdot +} \rightarrow ArO^{\cdot} + H^{+}\ (solvent)} \tag{3a}$$

$$\mathrm{ArOH^{\cdot +} + Cl^{-} \rightarrow products} \tag{3b}$$

This then raises the question about the influence of solvent properties and solute structure on the mechanism and kinetics of all these reactions.[19] The present study was initiated in order to obtain a deeper insight into the mechanism of electron transfer from various substituted phenols to parent ions of non-polar solvents. Such a study of phenols involving electron-withdrawing and -donating substituents compared to phenols with sterically hindered groups (Fig. 1) ought also to provide information about the stability and reactivity of the corresponding radicals and radical cations.

Experimental

Pulse radiolysis

The liquid samples were irradiated with high energy electron pulses (1 MeV, 15 ns duration) generated by a pulse transformer type accelerator ELIT (Institute of Nuclear Physics, Novosibirsk, Russia). The dose delivered per pulse was measured with an electron dosimeter and was usually around 100 Gy. Detection of the transient species was carried out using an optical absorption set-up consisting of a pulsed xenon lamp (XBO 900, Osram), a Spectra Pro-500 monochromator (Acton Research Corporation), an IP28 photomultiplier (Hamamatsu Photonics) and a 1GHz digitizing oscilloscope (TDS 640, Tektronix). Further details of this equipment are given elsewhere.[16]

Unless stated otherwise, the pulse radiolysis experiments were performed in nitrogen-saturated solutions of n-butyl chloride, 1,2-dichloroethane, n-dodecane and cyclohexane. Reactions with azide radicals were carried out in N_2O-saturated aqueous solutions at pH 1. The solutions were continuously passed through the sample cell with a path length of 1 cm.

Data analysis

The lifetimes τ of the phenol radical cations (Tables 1 and 2) were obtained from simple first-order exponential regression of the experimental time profiles.

The corresponding rate constants k_{3a} for the deprotonation of phenol radical cations were obtained by simulating the concentration *vs.* time profiles based on a reaction mechanism taking into account the elementary reactions involved. This was done using a program we wrote ourselves utilizing ACUCHEM[20] to solve rate equations (Table 1). This procedure was also used to determine the absorbance ratio between $\mathrm{ArOH^{\cdot +}}$ and $\mathrm{ArO^{\cdot}}$ at distinct wavelengths. The procedure includes the rapid formation of both species according to reactions (2a) and (2b), the decay of $\mathrm{ArOH^{\cdot +}}$ due to reactions (3a) and (3b), and the delayed formation of $\mathrm{ArO^{\cdot}}$ *via* reaction (3a). Using a scheme consisting of this set of reactions, the rate constants and yields were obtained by solving the corresponding rate equations. Thus for the particular example of n-butyl chloride as solvent, the rate equations mainly considered are as follows.

$$\begin{aligned} \mathrm{d}/\mathrm{d}t[\mathrm{ArOH^{\cdot +}}] &= k_{2b}[\mathrm{n\text{-}C_4H_9Cl^{\cdot +}}][\mathrm{ArOH}] \\ &\quad - k_{3a}[\mathrm{ArOH^{\cdot +}}] - k_{3b}[\mathrm{ArOH^{\cdot +}}][\mathrm{Cl^-}] \\ \mathrm{d}/\mathrm{d}t[\mathrm{ArO^{\cdot}}] &= k_{2b}[\mathrm{n\text{-}C_4H_9Cl^{\cdot +}}][\mathrm{ArOH}] \\ &\quad + k_{3a}[\mathrm{ArOH^{\cdot +}}] - 2k_{6d}[\mathrm{ArO^{\cdot}}]^2 \end{aligned}$$

These equations are similar in all the solvents studied here for all the phenols. Yields and molar absorption coefficients (ε) were determined using G values for free ions in solvents.[17,21] The $\varepsilon_{\max}$ values of phenoxyl radicals (Table 3) were obtained from transient spectra of the radicals under alkaline aqueous conditions in the presence of sodium azide. Here the concentration of the azide anions directly determines the concentration of phenoxyl radicals.[21–23]

Chemicals

All the phenols studied were commercially available (Merck) except for 4-$\mathrm{NMe_2}$-ArOH, which was synthesized as described in the literature.[24] The product was purified using chromatography and crystallization techniques. The solvents from Aldrich Sigma were of HPLC spectroscopy grade. All solvents were checked spectroscopically before use. The studies in aqueous solutions were performed in purified water (Millipore, Milli-Q plus system).

Quantum chemical approach

Using the semi-empirical PM3[25] and the density functional theory hybrid B3LYP[26] with 6-31G(d) basis set methods, geometrical and quantum chemical parameters of phenols were calculated by means of the Gaussian 94W program (Table 4).

Published on 06 October 2000. Downloaded by SUNY GENESEO on 22/10/2014 18:52:59.

Table 1 Kinetic and spectral parameters of phenol radical cations and phenoxyl radicals measured in n-butyl chloride

Phenols	$ArOH^{\bullet +}$ λ_{max} /nm	$ArOH^{\bullet +}$ τ^{a} /μs	$ArOH^{\bullet +}$ $k_{3a}{}^{b}$ /10^{6} s^{-1}	$ArOH^{\bullet +}$ $\varepsilon_{max}{}^{c}/10^{4}$ dm^{3} mol^{-1} cm^{-1}	$ArO^{\bullet}$ λ_{max} /nm
ArOH	440	0.27	4.0	—	400
4-NO_2-ArOH	510	0.23	4.0	0.29	430
4-CN-ArOH	480	0.11	9.0	7.29	440
4-Cl-ArOH	460	0.32	2.0	2.90	420
4-MeO-ArOH	450	0.34	3.0	2.48	410
4-NH_2-ArOH	450	0.68	0.9	0.34	440
4-NMe_2-ArOH	470	1.16	0.7	—	420
3-NMe_2-ArOH	500	1.27	0.7	3.51	460
4-Me-ArOH	430	0.42	1.5	2.88	400
DtBMeP	440	0.48	1.5	—	400
IRGANOX-1076®	450	0.37	2.0	—	370
4-MeO-ArSH[d]	570	0.21	5.0	5.34	520

[a] The errors of the lifetimes are within ±5%. [b] Obtained from kinetic simulations as described in the text. The errors of the rate constants are within ±10%. [c] The errors are within ±10%. [d] Oxygen saturated and the radicals formed here are of the type $ArS^{\bullet}$.

Table 2 Kinetic and spectral parameters for transient species formed during the pulse radiolysis of phenols in various solvents[ab]

	n-Dodecane ($\varepsilon = 2.01$; $\eta = 1.38$)			Cyclohexane ($\varepsilon = 2.02$; $\eta = 0.89$)			n-Butyl chloride ($\varepsilon = 7.39$; $\eta = 0.42$)			1,2-Dichloroethane ($\varepsilon = 10.19$; $\eta = 0.78$)		
	$ArOH^{\bullet +}$		$ArO^{\bullet}$	$ArOH^{\bullet +}$		$ArO^{\bullet}$	$ArOH^{\bullet +}$		$ArO^{\bullet}$	$ArOH^{\bullet +}$		$ArO^{\bullet}$
Phenol	λ_{max} /nm	τ /ns	λ_{max} /nm	λ_{max} /nm	τ /ns	λ_{max} /nm	λ_{max} /nm	τ /ns	λ_{max} /nm	λ_{max} /nm	τ /ns	λ_{max} /nm
ArOH	430	350	400	430	530	400	440	270	400	430	270	400
4-MeO-ArOH	440	330	410	440	460	410	450	340	410	440	320	410
4-Cl-ArOH	460	320	420	450	330	410	460	320	420	460	290	420
DtBMeP	450	270	400	440	610	400	440	480	400	440	350	400
4-MeO-ArSH[c]	570	210	520	570	220	510	570	210	520	570	310	520

[a] The errors of the lifetimes are within ±5%. [b] ε = relative permittivity at 25 °C; η = viscosity in mPa at 25 °C. [c] Oxygen saturated and the radicals formed are of the type $ArS^{\bullet}$.

Table 3 Kinetic and spectral parameters of phenoxyl radicals in aqueous solution

Phenol	$ArO^{\bullet}$ λ_{max}/nm	ε_{max} /10^{3} dm^{3} mol^{-1} cm^{-1}	Decay rate constant $(2k_{6d})^{a}$ /10^{8} dm^{3} mol^{-1} s^{-1}
4-MeO-ArOH	420	5.13	5.65
4-NO_2-ArOH	490	0.78	1.18
4-CN-ArOH	440	1.80	4.95
4-Cl-ArOH	420	3.72	2.76
4-NH_2-ArOH	320	0.79	1.00
	440	0.73	
3-NMe_2-ArOH	360	1.60	1.99
	490	2.18	
4-Me-ArOH	400	2.30	46.66
4-MeO-ArSH[b]	330	9.24	35.00
	530	5.93	

[a] The errors are within ±5%. [b] The radicals formed here are of the type $ArS^{\bullet}$.

Table 4 Density functional B3LYP/6-31G(d) and semiempirical PM3 calculated quantum chemical parameters of phenol radical cations in the gas phase and in n-C_4H_9Cl ($\varepsilon = 8$) approximated with Onsager reaction field (SCRF = Dipole) model in comparison with the experimentally obtained lifetimes, τ(ns), of the phenol radical cations in n-C_4H_9Cl (BuCl)

Phenols	τ/ns (expt.)[a]	*D* (DFT Debye)	*S*(O) (DFT vacuum)	*S*(O) (DFT BuCl)	*S*(O) (PM3 vacuum)	Δq(OH) (DFT vacuum)	Δq(OH) (DFT BuCl)	Δq(OH) (PM3 vacuum)
ArOH	270	1.46	0.197	0.201	0.186	0.213	0.213	0.223
4-MeO-ArOH	340	0.45	0.151	0.153	0.139	0.172	0.176	0.167
4-NO_2-ArOH	230	8.76	0.204	0.242	0.198	0.203	0.241	0.227
4-CN-ArOH	110	5.61	0.170	0.204	0.175	0.187	0.204	0.205
4-Cl-ArOH	320	3.68	0.168	0.189	0.124	0.187	0.203	0.162
4-NH_2-ArOH	680	3.37	0.133	0.118	0.086	0.161	0.136	0.115
4-NMe_2-ArOH	1160	2.42	0.110	0.103	0.072	0.140	0.133	0.098
3-NMe_2-ArOH	1270	2.04	0.005	0.003	−0.039	0.089	0.084	0.070
4-MeO-ArSH[b]	210	0.36	0.305	0.302	0.670	0.330	—	0.549

[a] The errors of the lifetimes are within ±5%. [b] The atomic spin density is calculated at sulfur and is denoted as *S*(S), and the difference in Mulliken charges denoted as Δq(SH) is calculated at the thiyl (–SH) group.

View Article Online

Published on 06 October 2000. Downloaded by SUNY GENESEO on 22/10/2014 18:52:59.

The solvent effect was taken into account by employing the Onsager self-consistent reaction field model (SCRF = Dipole)[27,28] for the structure optimized in vacuum at the B3LYP/6-31G(d) level.

Results

The interaction of ionizing radiation with non-polar solvents results in the generation of σ-type radical cations (parent cations) which are metastable in the nanosecond timescale. The ion–molecule reaction with a phenolic solute eqn. reaction (2) is an exergonic reaction driven by a free energy which can be expressed by the ionization potential difference between solvent and solute. The corresponding gas phase ionization potentials[21] of interest are: $IP_{gas} = 9.50$ eV for cyclohexane ($c\text{-}C_6H_{12}$), 9.60 eV for n-dodecane ($n\text{-}C_{12}H_{26}$), 10.7 eV for n-butyl chloride ($n\text{-}C_4H_9Cl$), and 11.04 eV for 1,2-dichloroethane ($ClCH_2CH_2Cl$), and for phenols, IP_{gas} around 8.0 to 9.0 eV. Therefore, in nearly every case diffusion-controlled rate constants were expected.

Electron transfer in n-butyl chloride

In the absence of any solute, the parent radical cations of n-butyl chloride initially generated by the electron pulse show broad absorption of 300–500 nm as reported.[16] The lifetime of the these radical cations is approximately 150 ns.

When a solute (phenols, ArOH) is added, the absorption band of the solvent disappears and a solute transient species is generated, indicating that electron transfer has occurred. As shown in Fig. 2(a), the transient optical absorption spectrum obtained during the pulse radiolysis of a nitrogen-saturated solution of 0.01 mol dm^{-3} 4-chlorophenol (4-ClArOH) in $n\text{-}C_4H_9Cl$, showed absorption bands at 310, 420 and 460 nm. These bands are observed immediately after the pulse. Analysis of the time profiles at these wavelengths revealed the band at 420 nm to be much longer-lived than those at 460 and 310 nm (Fig. 2(a), inset), the latter band in particular representing a strong superposition. This suggests the presence of at least two different species, assumed to be the phenol radical cation and the phenoxyl radical.[16] Moreover it is interesting to note that the phenoxyl radical absorption, clearly observable at 420 nm, is also formed very rapidly (within our time-resolution, *cf.* Fig. 2(a)), which illustrates that this species is formed almost instantaneously along with the cations. This type of behaviour is observed for all the phenols studied here, including 4-methoxythiophenol (4-MeO-ArSH), under identical conditions of dose and concentration. The spectral and kinetic parameters for the transient species formed during the pulse radiolysis of unsubstituted phenol, some phenols having electron-withdrawing (-nitro, -cyano and -chloro) and electron-donating (-methyl, -methoxy, -amino and -*N*,*N*-dimethylamino) substituents, along with phenols bearing sterically hindering groups (*tert*-butyl and long-chain fatty acid ester) and 4-methoxythiophenol, are given in Table 1.

Surprisingly, for all the phenols studied here, it was found that the electron transfer occurs *via* two distinct pathways, synchronously generating the phenol radical cations ($ArOH^{\cdot+}$), reaction (2a) and phenoxyl radicals ($ArO^{\cdot}$), reaction (2b).

When analysing the fate of the rapidly formed transients, it was found that the delayed additional generation of the phenoxyl radicals occurs along with the deprotonation of the phenol radical cations at a rate constant $k_{3a} = 1\text{–}5 \times 10^6\ s^{-1}$, reaction (3a). Studying the corresponding time profiles, this can be seen as the decay of phenol radical cations along with the superposition of the delayed formation of phenoxyl radicals.

The phenol radical cations decay by pure first-order kinetics. Hence, the main decay pathway ought to be deprotonation leading to the generation of phenoxyl radicals.[2] The lifetimes υ of the radical cations correlate well with the rates of decay k_{3a} (determined by kinetic simulations which are explained in detail in the data analysis section) as shown in Table 1.

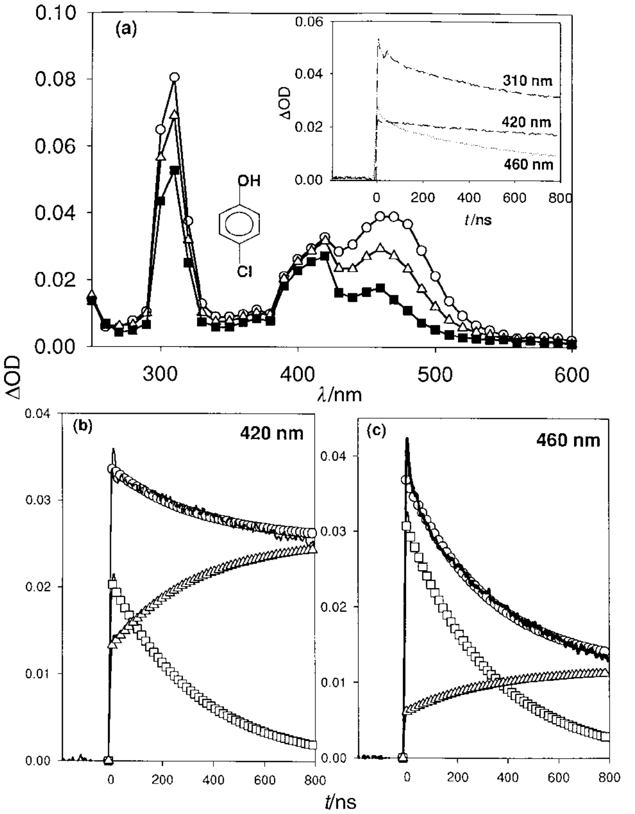

Fig. 2 (a) Transient optical absorption spectra obtained in the pulse radiolysis of a nitrogen-saturated solution of 0.01 mol dm^{-3} 4-Cl-ArOH in $n\text{-}C_4H_9Cl$ after (○) 10, (△) 100 and (■) 500 ns. The inset shows the time profiles of a nitrogen-saturated solution of 0.01 mol dm^{-3} 4-Cl-ArOH in $n\text{-}C_4H_9Cl$ at different wavelengths. The simulations of the time profiles (○) obtained using the ACUCHEM program are as shown at 420 nm (b) and at 460 nm (c) with the solid line being the original measurement curve. The additional curves represent the results of simulation for the formation of the phenoxyl radicals (△) and the decay of the phenol radical cations (□).

Returning to the phenomenon of rapid formation of the $ArOH^{\cdot+}$ and $ArO^{\cdot}$, the ratio of the yields of the transient species is of great interest. Although molar absorption coefficients are only directly available in the case of $ArO^{\cdot}$ (see below), the transient ratio can be estimated from kinetic simulation of the experimental time profiles using the ACUCHEM[20] program. As already mentioned, the measured optical absorption time profiles represent considerable superposition of both species and can therefore be interpreted by the simulation operation as shown, *e.g.* in Fig. 2(b) and (c) for calculations made for 420 and 460 nm absorptions. Here, either the phenoxyl radical or the phenol radical cation is by far the most dominant species, but in each case the slow background is caused by phenoxyl radicals. From analysis of the $ArOH^{\cdot+}$ decay as well as the delayed formation of $ArO^{\cdot}$, the ratio of the fast formation of the two transients by electron transfer, reactions (2a) and (2b) can be concluded to be about 50% for each reaction channel. This means that both pathways (2a) and (2b) have the same reaction probability.

In addition to the $n\text{-}C_4H_9Cl^{\cdot+}$ species, the radiolysis of $n\text{-}C_4H_9Cl$ also generates butyl radicals ($n\text{-}C_4H_9^{\cdot}$) which could conceivably react with the phenols by a hydrogen atom abstraction, reaction (3c).

$$n\text{-}C_4H_9^{\cdot} + ArOH \rightarrow ArO^{\cdot} + n\text{-}C_4H_{10}; \quad k_{3c} < 10^5\ dm^3\ mol^{-1}\ s^{-1} \qquad (3c)$$

View Article Online

Published on 06 October 2000. Downloaded by SUNY GENESEO on 22/10/2014 18:52:59.

In the timescale of the analysis (up to 20 μs) this does not occur, as the rate constant of this reaction is very slow compared to $k_{2a,b}$.[13] In contrast to this, with aromatic thiols, the analogous H-abstraction was found to be faster, exhibiting a rate constant of around 10^8 dm^3 mol^{-1} s^{-1}.[29] Hence the thiophenol 4-MeO-ArSH was studied in oxygen-saturated samples where less reactive species such as butylperoxyl radicals are formed, thus preventing the formation of thiyl radicals from a non-ionic channel. All other phenols were studied in a nitrogen-saturated environment.

The transient species were identified by using additional scavengers such as ethanol (C_2H_5OH) and triethylamine (TEA). Both quench the phenol radical cations, albeit in different ways. Transient optical absorption spectra of nitrogen-saturated solutions of 0.1 mol dm^{-3} ethanol in 0.01 mol dm^{-3} of 4-Cl-ArOH in n-C_4H_9Cl showed the complete disappearance of the short-lived band at 460 nm, with a relatively small decrease, *ca.* 30%, at 310 nm, while the peak at 420 nm corresponding to the long-lived species showed little or no change (Fig. 3). Ethanol deprotonates the phenol radical cation in a bimolecular reaction ($k_{4a} = 6 \times 10^8$ dm^3 mol^{-1} s^{-1}), converting it into a phenoxyl radical, eqn. (4a).

$$\mathrm{ArOH^{\cdot +} + C_2H_5OH \rightarrow ArO^{\cdot} + C_2H_5OH_2{}^{+}} \qquad (4a)$$

Hence the transient optical absorption spectra in the presence of 0.1 mol dm^{-3} ethanol ought only to be due to phenoxyl radicals. The difference between the spectra in the absence and presence of ethanol mainly gives the spectrum of the phenol radical cations. The peak at 460 nm was thus identified as being due to the phenol radical cations. The band at 420 nm was attributed to the long-living phenoxyl radicals as they were hardly affected by ethanol—a supposition which is also in accordance with the literature.[30] The peak at 310 nm is partially quenched and represents a substantial superposition of both the radical cations and the radicals. The small decrease in absorption at 420 nm is attributed to the fact that ethanol also competes with the charge transfer from the parent solvent radical cations, thereby scavenging them, eqn. (4b).

$$\mathrm{n\text{-}C_4H_9Cl^{\cdot +} + C_2H_5OH \rightarrow n\text{-}C_4H_8Cl^{\cdot} + C_2H_5OH_2{}^{+}} \qquad (4b)$$

Consequently, ethanol partially prevents the formation of phenol radical cations, eqn. (2a) and also the direct formation of phenoxyl radicals, eqn. (2b). Analogous results were obtained for all the phenols studied. The wavelengths of absorption for the radical cations and radicals of the corresponding phenols are given in Table 1.

In comparison to this, the effect of a comparatively small amount of TEA (0.002 mol dm^{-3}) was more simple, as TEA only reacts with the phenol radical cations by electron transfer, eqn. (5).

$$\mathrm{ArOH^{\cdot +} + TEA \rightarrow ArOH + TEA^{\cdot +}} \qquad (5)$$

Thus only the phenol radical cations were scavenged (Fig. 3). After the addition of just 0.002 mol dm^{-3} TEA to 0.01 mol dm^{-3} 4-Cl-ArOH in n-C_4H_9Cl, the band at 460 nm completely disappears, thereby confirming the transient species as phenol radical cations, eqn. (5). The bands at 320 and 420 nm are due to the phenoxyl radicals. The decrease in their intensities is due to the lack of formation of phenoxyl radicals by deprotonation of phenol radical cations, eqn. (3a). Additionally a small absorption at around 360 nm is observed which is due to TEA radical cations which confirms the fact that this quenching of phenol radical cations is by electron-transfer reaction (5).

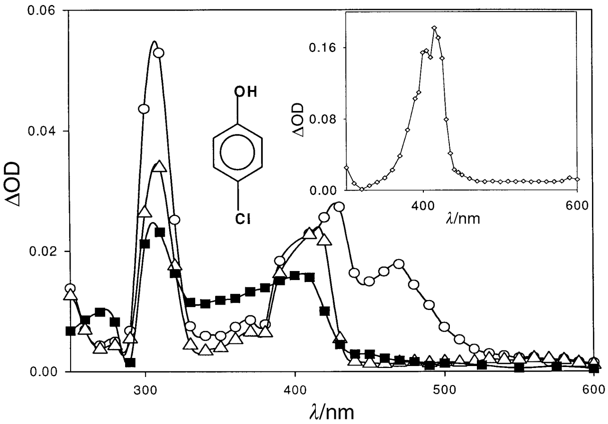

Fig. 3 Transient optical absorption spectra obtained in the pulse radiolysis of a nitrogen-saturated solution of 0.01 mol dm^{-3} 4-Cl-ArOH in n-C_4H_9Cl (○) after 100 ns, in the presence of (△) 0.1 mol dm^{-3} EtOH and in the presence of (■) 0.002 mol dm^{-3} TEA. The inset is of 0.01 mol dm^{-3} 4-Cl-ArOH in water in the presence of 1 mol dm^{-3} NaN_3 at pH 11 under N_2O atmosphere.

In order to verify the spectrum of phenoxyl radicals (ArO$^{\cdot}$), pulse radiolysis studies of the phenols were also performed in aqueous alkaline (pH 11) solution under N_2O atmosphere in the presence of sodium azide. Under these conditions the solvated electrons are converted to OH$^{\cdot}$, reaction (6a) with the subsequent generation of azide radicals, reaction (6b). The azide radicals then react with the phenolate anions leading to the quantitative formation of phenoxyl radicals and azide anions (6c)[23] (Fig. 3, inset). The absorption peaks of the phenoxyl radicals are comparable with those obtained under other conditions, with the exception of one or two cases where they are slightly red-shifted in comparison to those obtained in n-C_4H_9Cl, as expected due to the surrounding polar aqueous medium. The phenoxyl radicals decay by second-order kinetics, reaction (6d), and the rate constants are as shown in Table 3 along with the wavelengths of maximum absorption and the molar absorption coefficients of ArO$^{\cdot}$.

$$\mathrm{N_2O + e_{aq}{}^{-} \rightarrow OH^{\cdot} + OH^{-} + N_2} \qquad (6a)$$

$$\mathrm{OH^{\cdot} + N_3{}^{-} \rightarrow N_3{}^{\cdot} + OH^{-}} \qquad (6b)$$

$$\mathrm{ArO^{-} + N_3{}^{\cdot} \rightarrow N_3{}^{-} + ArO^{\cdot}} \qquad (6c)$$

$$\mathrm{2ArO^{\cdot} \rightarrow products} \qquad (6d)$$

Assuming nearly identical behaviour in water and in nonpolar solvents, along with the molar absorption coefficients of ArO$^{\cdot}$, the ε values of the phenol radical cations were also estimated (see Table 1). This was done using the ratio of the rapid and delayed formed phenoxyl radicals and internal calibration to the ArOH$^{\cdot +}$ based on the kinetic simulation procedure described above (*cf.* Fig. 2(b)).

Electron transfer in 1,2-dichloroethane

Pure 1,2-dichloroethane also forms parent ions upon irradiation[21] under identical conditions as described for n-C_4H_9Cl. The presence of an additional chlorine atom increases the ionization potential as compared to n-butyl chloride and makes it an efficient electron acceptor. After radiolysis, the absorption spectra of the pure solvent taken under comparable conditions as described for n-butyl chloride showed higher absorbances in the region 300–600 nm because of its higher G_{fi} value.[21] The 1,2-dichloroethane radical cation ($ClCH_2CH_2Cl^{\cdot +}$) as the primary species exhibits a decay lifetime of 210 ns. The subsequent electron-transfer processes behaved quite analogously to the situation described for n-butyl chloride.

Here also it was found that the electron-transfer process occurs in two distinct ways, synchronously generating the phenol radical cations and the phenoxyl radicals immediately after pulse irradiation. This is clearly apparent from Fig. 4 for the example of phenol (0.01 mol dm^{-3}) dissolved in 1,2-dichloroethane. The bands at 400 and 430 nm are attributed to the phenoxyl radicals and the phenol radical cations,

Published on 06 October 2000. Downloaded by SUNY GENESEO on 22/10/2014 18:52:59.

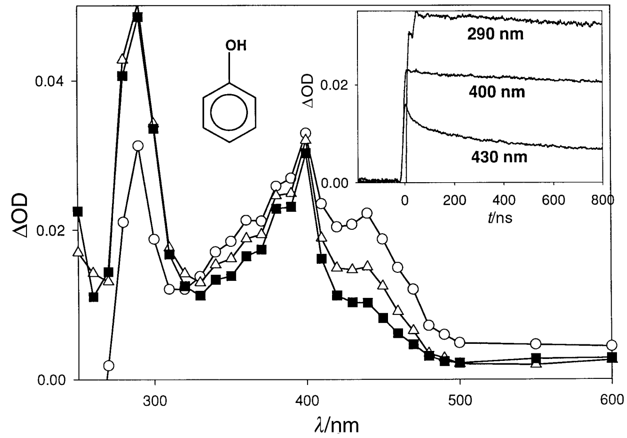

Fig. 4 Transient optical absorption spectra obtained in the pulse radiolysis of a nitrogen-saturated solution of 0.01 mol dm^{-3} ArOH in 1,2-dichloroethane after (○) 10, (△) 100 and (■) 500 ns. The inset shows the time profiles at different wavelengths.

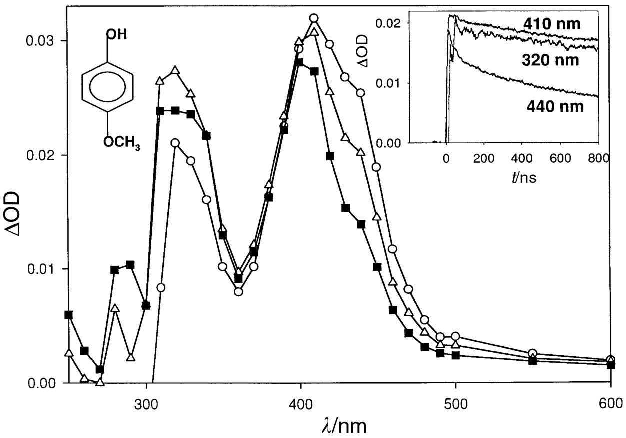

Fig. 5 Transient optical absorption spectra obtained in the pulse radiolysis of a nitrogen-saturated solution of 0.01 mol dm^{-3} 4-MeO-ArOH in oxygen in cyclohexane containing 0.1 mol dm^{-3} carbontetrachloride after (○) 30, (△) 100 and (■) 500 ns. The inset shows the time profiles at different wavelengths.

respectively. The band at 290 nm is due to the superposition of the phenol radical cations and phenoxyl radicals. Assignment was carried out using 0.1 M EtOH as a positive charge scavenger, based on explanations given earlier. As expected, such behaviour was also observed for all the phenols studied and the results are shown in Table 2. The unsubstituted phenol (ArOH) has the shortest lifetime (240 ns) for the phenol radical cations, while DtBMeP (350 ns) and 4-MeO-ArOH (320 ns) are longer lived.

Electron transfer in cyclohexane

The transient optical absorption spectra of the phenol transients obtained under identical conditions of concentration and electron pulse irradiation in cyclohexane were quite similar to those in the other solvents mentioned above. The parent cyclohexane radical cations show absorptions in the range 400–600 nm.[19] The low intensity of the phenol transient absorptions are due to the low G_{fi} value[21] (0.015 μmol J^{-1}) of the free solvent radical cation.

When analysing the fate of the parent radical cations in cyclohexane, many processes need to be considered.[19] In the presence of carbon tetrachloride (CCl_4) as electron scavenger, reaction (7) (added to avoid phenolate anion formation), the situation becomes much clearer and hence reduces the mechanism to the electron-transfer reactions already discussed, reactions (2a) and (2b) and the subsequent deprotonation, reaction (3a).

$$CCl_4 + e_{\mathrm{solv}}^{-} \rightarrow Cl^{-} + CCl_3^{\cdot} \qquad (7)$$

In cyclohexane, the simultaneous formation of phenol radical cations and the phenoxyl radicals is illustrated using the example of 0.01 mol dm^{-3} 4-methoxyphenol (Fig. 5). The species identified (Fig. 5, inset) were found to absorb at 410 nm (phenoxyl radicals) and 440 nm (phenol radical cations), with the superposition of the two species at 320 nm. Here, too, the simultaneous formation of the two phenol transients is observed with the same yield ratio of 1 : 1.

The ArOH$^{\cdot+}$ lifetimes obtained for all phenols investigated compared to those found using the alkyl chloride solvents are given in Table 2.

Electron transfer in n-dodecane

In relation to the other solvents, n-dodecane should be regarded as similar to cyclohexane, albeit with a viscosity nearly three times higher. Carbon tetrachloride (0.1 mol dm^{-3}) is added to scavenge electrons and thereby avoid the superposition of electron reaction products in the spectra. n-$C_{12}H_{26}^{\cdot+}$ itself is known to have an optical absorption maximum at around 800 nm.[19b] In these primary solvent radical cations, the charge is expected to be distributed in the long hydrocarbon chain among the methylene (–CH_2–) groups.

Under analogous conditions, the simultaneous formation of phenol radical cations and phenoxyl radicals occurs, which is demonstrated here by the example of spectra and time profiles of 0.01 mol dm^{-3} 4-Cl-ArOH in n-dodecane in the presence of 0.1 mol dm^{-3} carbon tetrachloride (Fig. 6). The distinct electron-transfer phenomenon was also observed in this solvent. The spectra are identical to those taken in n-butyl chloride and, surprisingly, the decay of ArOH$^{\cdot+}$ proceeds at nearly the same rate as found for the other solvents, showing that reaction (3a) is independent of viscosity (Table 2).

Discussion

Mechanistic considerations

The salient feature of all the above observations is the synchronous generation of phenol radical cations and phenoxyl radicals almost immediately after pulse irradiation. This can be vividly understood from the illustration in Fig. 7, which is designed to provide a simplified microscopic picture of the mechanism. Hence the solvent parent radical cation can meet the aromatic ring in a diffusion-controlled manner in various

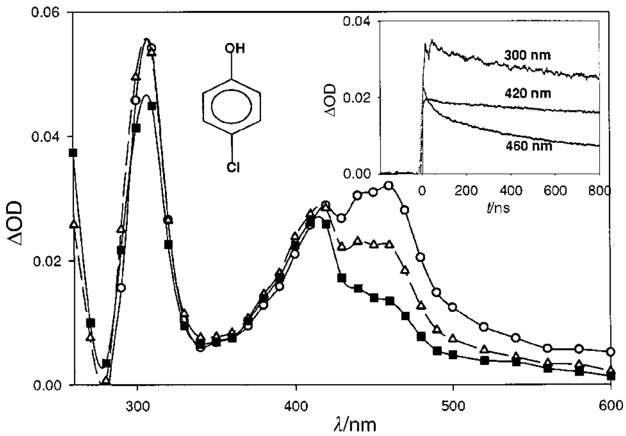

Fig. 6 Transient optical absorption spectra obtained in the pulse radiolysis of a nitrogen-saturated solution of 0.01 mol dm^{-3} 4-Cl-ArOH in n-dodecane containing 0.1 mol dm^{-3} carbontetrachloride after (○) 30, (△) 100 and (■) 500 ns. The inset shows the time profiles at different wavelengths.

Published on 06 October 2000. Downloaded by SUNY GENESEO on 22/10/2014 18:52:59.

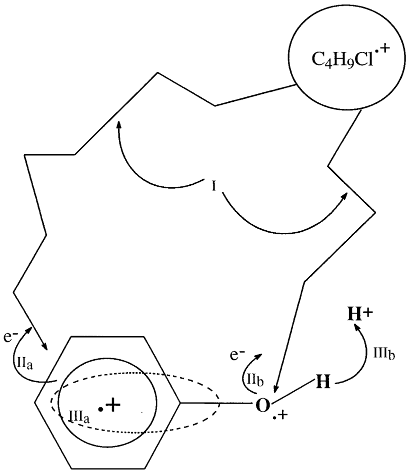

Fig. 7 Mechanism of electron transfer between the n-C_4H_9Cl radical cation and phenol.

constellations (I) where diffusion should be regarded as a normal and relatively slow process.

After the diffusive encounter, electron transfer (II) happens extremely rapidly and apparently locally. Thus electron transfer from the aromatic ring to the solvent cation (II_a) occurs, while the positive charge is stabilized within the aromatic system with the involvement of substituents on the ring (III_a). The other kind of attack leads to interaction between the phenolic oxygen atom and the solvent radical cation (II_b), followed by immediate deprotonation (III_b) certainly occurring before charge distribution occurs throughout the molecule. The products are phenoxyl radicals (III_b). Hence it is evident that even for such small solute molecules as the phenols, the ion–molecule reaction (2) can proceed *via* two different channels involving encounter between the parent ion and the aromatic ring as well as the hydroxy group of the solute molecule. Hence, such different encounter situations lead to the synchronous formation of phenol radical cations, reaction (8a) and phenoxyl radicals, reaction (8b), formulated for n-butyl chloride as solvent and for any phenol.

$$\longrightarrow [\text{HO–Ar}\cdots{}^{\cdot+}\text{ClC}_4\text{H}_9] \longrightarrow [\text{Ar}^{\cdot+}\text{OH}\cdots\text{ClC}_4\text{H}_9] \longrightarrow {}^{\cdot+}\text{ArOH} + \text{ClC}_4\text{H}_9 \qquad (8a)$$

$$\text{Ar–OH} + \text{C}_4\text{H}_9\text{Cl}^{\cdot+}$$

$$\longrightarrow [\text{Ar–OH}\cdots{}^{+\cdot}\text{ClC}_4\text{H}_9] \longrightarrow [\text{Ar–O}^{\cdot+}\text{H}\cdots\text{ClC}_4\text{H}_9] \longrightarrow \text{ArO}^{\cdot} + \text{H}^+(\text{ClC}_4\text{H}_9) \qquad (8b)$$

Additionally, the latter effect may very well be due to an energetically favoured electron-transfer geometry at the phenolic group.[3] Thus, depending on the type of encounter geometry, two different kinds of products are obtained. For the case of reaction (8b), this is supported by molecular orbital (MO) calculations, which have shown a favoured distance of 1.8 Å between the chlorine atom of n-C_4H_9Cl and the phenolic proton, resulting in a preferential geometry for the charge transfer.[2,31]

Overall, diffusion is the slowest process and therefore determines the rate of the process. Hence, from the decay of the parent ions (n-$C_4H_9Cl^{\cdot+}$) and the growth of the products ($ArOH^{\cdot+}$ and $ArO^{\cdot}$) a rate constant k_2 of about 2×10^{10} dm^3 mol^{-1} s^{-1} was calculated for different phenol concentrations, which is slightly higher than actual diffusion control caused by a residue of the original inhomogeneous distribution of radiation-generated species.[32]

The simultaneous generation of phenol radical cations and phenoxyl radicals is observed in all the types of phenols studied here, proceeding in a product ratio of about one to one. In relation to this, questions arose on the specific influence of a number of parameters such as the electronic structure of the phenol, the concentration of these solutes, the type of solvent *etc*. Therefore, we investigated the influence of these parameters on the electron-transfer phenomenon and the stability of the resulting metastable phenol radical cations.

Influence of the phenol structure on the electron transfer

The electronic structure of the phenol depends on the nature of the substituents on the aromatic ring. The phenols studied here can be classified into the following categories *viz.*:

Those with electron-withdrawing substituents (*e.g.* nitro-, cyano-, and chloro-substitution in the *para*-position);

Those with electron-donating substituents (*e.g.* amino-, dimethylamino-, methoxyl-, methyl-groups in the *para*-position);

Sterically hindered phenols substituted by *e.g. tert*-butyl groups and/or long-chain fatty acid residues.

The influence of molecular electronic effects on the electron-transfer mechanism, reactions (8a) and (8b) and the stability of the phenol radical cations was studied using these differently structured phenols. Interestingly, it is obvious that the electron transfer from the phenol to the solvent radical cation seems to be largely independent of the nature of the solute. Hence irrespective of the kind of phenol and its electronic structure, in all cases both kinds of transients (phenol radical cations and phenoxyl radicals) are produced synchronously and apparently to a comparable extent. Hence we can say that within the error limit of 10%, the electron transfer probability from the aromatic ring or from the phenoxyl group to the solvent parent ion is 50%. This is a clear result of all of our extended fit operations described above.

Solvent influence on electron transfer

The solvents studied here differ not only in their ionization potentials (IP_{gas}), but also in other physical properties such as relative permitivity (ε) and viscosity (η) (Table 2). 1,2-Dichloroethane has the highest relative permittivity while n-dodecane is at least three times more viscous than cyclohexane and the two alkyl chlorides. The conditions of the electron transfer, however, are controlled in a manner warranting the same mechanism and same reaction pathways.

Hence the results shown above clearly indicate that the synchronous formation of the two products, phenol radical cations and phenoxyl radicals, is not markedly affected by the solvent properties. Such a universal feature implies that the free electron transfer is independent of the type of non-polar solvent used. This is also true for much more polar solvents such as acetone,[33] where only the $ArOH^{\cdot+}$ deprotonation is affected, but not the electron transfer channels (8a) and (8b).

It should be borne in mind that the overall electron-transfer reaction (8) from solute phenol to solvent radical cation occurs in a diffusion-controlled manner while the actual electron-transfer step (II in Fig. 7) is extremely fast—being believed to proceed in the (sub)-femtosecond timescale. Therefore, under such conditions solvent physical parameters such as viscosity have little influence on this electron transfer step taking place in the different functional groups of the phenol molecule.

Concerning the increase in the phenol concentration, it was found that the absorbances of the transients at the respective wavelengths increase, indicating enhancement in the yields of the phenol radical cations and phenoxyl radicals (see inset in Fig. 2(a)). However, at higher solute concentration this seems to be disproportionate at the expense of $ArOH^{\cdot+}$, *i.e.* above 0.01 mol dm^{-3} phenol, the phenoxyl radical yield increases more than that of the phenol radical cations. This effect can be explained by the fact that, at high phenol concentrations

Published on 06 October 2000. Downloaded by SUNY GENESEO on 22/10/2014 18:52:59.

(>0.01 mol dm^{-3}), competition between the phenol and the radiolytically primarily formed H atoms in the solvent, generates additional phenoxyl radicals (*cf.* reactions (9a) and (9b)).[13]

$$\mathrm{H^{\bullet} + c\text{-}C_6H_{12} \rightarrow H_2 + c\text{-}C_6H_{11}^{\bullet}}; \quad k_{9a} = 10^6\ \mathrm{s^{-1}} \qquad (9a)$$

$$\mathrm{H^{\bullet} + ArOH \rightarrow H_2 + ArO^{\bullet}}; \quad k_{9b} = 10^6\ \mathrm{s^{-1}} \qquad (9b)$$

Relation between phenol structure and the stability of $\mathrm{ArOH^{\bullet +}}$

In contrast to the electron-transfer phenomenon (8a, reactions and (8b), the decay kinetics of the phenol radical cations certainly depends on the electronic effects. The fate of the phenol radical cation can be inferred from the time profiles. The time profile of the radical cation formed under identical conditions of dose and concentration was compared for the different phenols. Thus it can be seen that the radical cation of 4-CN-ArOH undergoes the most rapid decay (110 ns, *cf.* also Table 1). The electronic and steric effects can be judged by looking at the lifetime profiles of the differently structured phenol radical cations. It is evident that the radical cations of phenols with electron-donating groups (4-NMe$_2$-ArOH) decay more slowly than those of phenols with electron-withdrawing groups (4-Cl–ArOH). This is because electron-donating groups such as -methoxy, -amino and -*N*,*N*-dimethylamino stabilize the radical cation while the electron-withdrawing groups like -nitro, -cyano and -chloro destabilize it. By contrast, radical cations of phenols with sterically hindering groups (DtBMeP and IRGANOX - 1076®) showed little difference in the rate of decay. This is reflected by the values of their lifetimes (Table 1). Generally, the large difference in the lifetimes indicates the strong electronic effect of the substituents. In sharp contrast to this, there is only a small steric effect. This may also be understood in terms of the inductive effect of the alkyl groups.

The deprotonation of the phenol radical cations in the non-polar surroundings seems to be mostly governed by intramolecular effects and represents an irreversible monomolecular decay reaction (3a) rather than the acid–base equilibria, reaction (10), reported to exist in protic and polar solvents.[15]

$$\mathrm{ArO^{\bullet} + H_3O^{+} \rightleftarrows ArOH^{\bullet +} + H_2O} \qquad (10)$$

Considering the electronic effects of the various *para*-substituents, a convincing correlation between the experimental lifetimes and the quantum chemical calculated spin density at the phenolic oxygen has been found for the monomolecular deprotonation of $\mathrm{ArOH^{\bullet +}}$ in non-polar media discussed herein.[34] In this manner, the spin density S(O) at the oxygen atom and the charge difference between the singlet ground state and the radical cation Δq(OH) at the hydroxy group of the radical cation were calculated and compared with the experimentally determined lifetimes τ (*cf.* Table 4).

As expected and already mentioned, phenols with electron-donating groups which stabilize the radical cation have long lifetimes. Based on the earlier discussion, the quantum chemical calculations show that these phenols (4-NMe$_2$-ArOH, 3-NMe$_2$-ArOH, 4- NH$_2$-ArOH and 4-Me-ArOH) have low values of S(O) and Δq(OH). In contrast, high values of S(O) and Δq(OH) are obtained for radical cations of phenols with electron-withdrawing groups (4-NO$_2$-ArOH, 4-Cl-ArOH, 4-CN-ArOH) with short lifetimes. Thus good correlation was obtained between S(O) and Δq(OH), and the lifetime of the phenol radical cations. This corroborates well with the experimental discussion mentioned earlier.

Radical cations of aromatic thiols[2] have been found to exhibit similar behaviour to the phenol cations. This is observed in this study using the example of 4-MeO-ArSH where the synchronous formation of thiol radical cations and thiyl radicals is also demonstrated. However, the radical cations of the aromatic thiols decay much faster than the phenol radical cations (Tables 1 and 2). This can be attributed to the fact that since the heteroatom sulfur has a higher electronegativity than oxygen, it causes more localization of charge leading to faster deprotonation.[2]

Analysing the effect of the type of solvent on the stability of the phenol radical cations, it should be stated that, for experimental reasons, we only had non-polar solvents at our disposal with a maximum relative permittivity of about 8.0. Within this limitation, we found that the solvent type rarely influences the decay kinetics of the phenols, and never more than to a very minor extent. In this respect, phenol radical cations of 4-Cl-ArOH have nearly identical lifetimes in all the solvents. This also holds for the radical cations of 4-MeO-ArSH and 4-MeO-ArOH in the various solvents except cyclohexane. The unsubstituted phenol (ArOH) shows identical lifetimes in the alkyl chlorides and apparently higher values in the solvents of alkane type. A genuine exception seems to exist for the phenol radical cations of DtBMeP, where the decay times vary between 270 and 610 ns (Table 2), which we are unable to interpret.

In general, however, within a relatively large error, it can be stated that the radical cations of the phenols show nearly identical decay kinetics in all the solvents used. This error which is reflected in the lifetimes of the phenol radical cations, is less ($\leqslant 5\%$) in a defined solvent. The variation in this error from solvent to solvent, however, does not influence our calculations. Additionally, it was found that the decay does not depend on the concentration of the phenol radical cation ($\mathrm{ArOH^{\bullet +}}$). All this supports the hypothesis that the main decay channel for the phenol radical cations is deprotonation, a unimolecular reaction which ought to be largely independent of the non-polar surroundings.

Concerning the error limit, the influence of solvent primary processes such as the early fragmentation of excited parent ions[19] may generate species of additional optical absorptions (olefin radical cations) which are not markedly involved in the reaction mechanism we analysed. However, such effects, and also that of added carbon tetrachloride as electron scavenger in the alkanes, only modifies the transient absorptions observed in different solvents to a small extent.

A dependence on phenol structure can also be seen in the case of phenoxyl radicals (Table 3). In aqueous solutions they were found to decay by second-order kinetics (Table 3) with $2k$ in the range $(1.0\text{–}6.0) \times 10^8$ dm^3 mol^{-1} s^{-1}. As expected, the thiophenoxyl radical of 4-MeO-ArSH decays much faster than the phenoxyls.

Conclusions

The pulse radiolytic study of phenols in non-polar solvents involved the analysis of two features *viz.* the free electron transfer from phenols to solvent radical cations and the stability of the phenol radical cations.

The results ascertained the importance of the role of geometry of encounter in the electron transfer from the solute phenol to the solvent radical cation. This was based on the evidence for the observation of synchronously formed phenol radical cations and phenoxyl radicals. This phenomenon was observed for phenols of very different electronic structure and was found to be hardly affected by the structure of the phenols or the non-polar solvents used. Although such a universality implies that the local electron transfer is a general effect of this type of ion–molecule reaction, it was only identified in the case of molecules able to form both metastable radical cations (electron transfer involving the aromatic moiety) and radical cations with extremely low stability (electron transfer from the phenolic OH group). To the best of our knowledge, this is the first time that such local, encounter-geometry-controlled electron transfer in relatively small molecules has been shown to be a general effect. This provides a basis for the general theo-

Published on 06 October 2000. Downloaded by SUNY GENESEO on 22/10/2014 18:52:59.

retical treatment of the free electron transfer from solute molecules to parent ions which obeys rules different from other well-known electron-transfer reactions such as the photosensitized electron transfer processes.[35] These interpretations are currently in progress.

As for the second topic, the stability of the phenol radical cations was found to be governed by the structural factors of the solute, with the electronic factors dominating over the steric. This was inferred from the investigations into the influence of a variety of *para*-substituents in the non-polar solvents. The deprotonation of the phenol radical cations here represents an irreversible unimolecular decay which is principally different from the acid–base equilibria observed in protic solvents.[14] The results were further substantiated by the quantum chemical studies.

References

1 R. Mehnert, O. Brede and W. Naumann, *Ber. Bunsen-Ges. Phys. Chem.*, 1982, **86**, 525.
2 R. Hermann, G. R. Dey, S. Naumov and O. Brede, *Phys. Chem. Chem. Phys.*, 2000, **2**, 1213.
3 G. R. Dey, R. Hermann, S. Naumov and O. Brede, *Chem. Phys. Lett.*, 1999, **310**, 137.
4 R. Mehnert, in *Radical Ionic Systems—Properties in Condensed Phases*, ed. A. Lund and M. Shiotani, Kluwer, Dordrecht, 1991, p. 231.
5 O. Brede, R. Mehnert and W. Naumann, *Chem. Phys.*, 1987, **115**, 279.
6 *Atmospheric Oxidation and Antioxidants*, ed. G. Scott, Elsevier, Amsterdam, 1993, vol. I and II.
7 W. Schnabel, *Polymer Degradation*, Hanser, München, 1992.
8 O. Brede and L. Wojnarovis, *Radiat. Phys. Chem.*, 1991, **37**, 537.
9 N. Getoff and S. Solar, *Radiat. Phys. Chem.*, 1988, **31**, 121.
10 S. Steenken and P. Neta, *J. Phys. Chem.*, 1982, **86**, 3661.
11 O. Brede, H. Orthner and R. Hermann, *Chem. Phys. Lett.*, 1994, **229**, 571.
12 (*a*) E. J. Land, G. Porter and E. Strachan, *Trans. Faraday Soc.*, 1961, **57**, 1885; (*b*) K. M. Bansal and R. W. Fessenden, *Radiat. Res.*, 1976, **67**, 1.
13 O. Brede, R. Hermann and R. Mehnert, *J. Chem. Soc., Faraday Trans., 1*, 1987, **83**, 2365.
14 (*a*) W. T. Dixon and D. Murphy, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 1221; (*b*) W. T. Dixon and D. Murphy, *J. Chem. Soc., Faraday Trans. 2*, 1978, **74**, 432.
15 F. G. Bordwell and J.-P. Cheng, *J. Am. Chem. Soc.*, 1991, **113**, 1736.
16 O. Brede, H. Orthner, V. E. Zubarev and R. Hermann, *J. Phys. Chem.*, 1996, **100**, 7097.
17 H. Mohan, R. Hermann, S. Naumov, J. P. Mittal and O. Brede, *J. Phys. Chem. A*, 1998, **102**, 5754.
18 T. A. Gadosy, D. Shukla and L. Johnston, *J. Phys. Chem. A*, 1999, **103**, 8834; H. Orthner, PhD Dissertation, University of Leipzig, 1995.
19 (*a*) R. Mehnert, O. Brede and W. Naumann, *J. Radioanal. Nucl. Chem.*, 1986, **101**, 307; (*b*) R. Mehnert, O. Brede and W. Naumann, *Ber. Bunsen-Ges. Phys. Chem.*, 1984, **88**, 71.
20 W. Braun, J. T. Herron and D. K. Kahaner, *Int. J. Chem. Kinet.*, 1988, **20**, 51.
21 Y. Tabata, Y. Ito and S. Tagawa, *CRC Handbook of Radiation Chemistry*, CRC Press, Boston, 1991, p. 103.
22 F. Busi, in *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*, ed. J. Baxendale and F. Busi, Reidel, Dordrecht, 1982, p. 417.
23 Z. B. Alfassi and R. H. Schuler, *J. Phys. Chem.*, 1985, **89**, 3359.
24 A. H. Blatt, *Org. Synth.*, 1941, Coll. Vol. I, 404.
25 J. P. P. Stewart, *J. Comput.-Aided Mol. Design*, 1990, **4**, 1.
26 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
27 M. W. Wrong, M. J. Frisch and K. B. Wiberg, *J. Am. Chem. Soc.*, 1991, **113**, 4776.
28 M. W. Wrong, K. B. Wiberg and M. J. Frisch, *J. Am. Chem. Soc.*, 1992, **114**, 1645.
29 M. Bonifacic, J. Weiss, S. A. Chandra and K.-D. Asmus, *J. Phys. Chem.*, 1985, **89**, 3900.
30 (*a*) E. J. Land and M. Ebert, *Trans. Faraday Soc.*, 1967, **63**, 1181; (*b*) E. J. Land and G. Porter, *Trans. Faraday Soc.*, 1963, **59**, 2016.
31 R. Hermann, S. Naumov and O. Brede, *THEOCHEM*, 2000, **532**, 69.
32 A. Hummel, in *Radiation Chemistry-Principles and Applications*, ed. Farhataziz and M. A. Rodgers, VCH, New York, 1987, p. 97.
33 R. Lomoth, S. Naumov and O. Brede, *J. Phys. Chem.*, 1999, **103**, 2641.
34 R. Hermann, S. Naumov, G. R. Mahalaxmi and O. Brede, *Chem. Phys. Lett.*, 2000, **324**, 265.
35 J. G. Kavarnos, in *Fundamentals of Photoinduced Electron Transfer*, VCH, New York, 1993, p. 287.